

THE CHEMCOAL PROCESS
FOR
LOW TEMPERATURE CONVERSION

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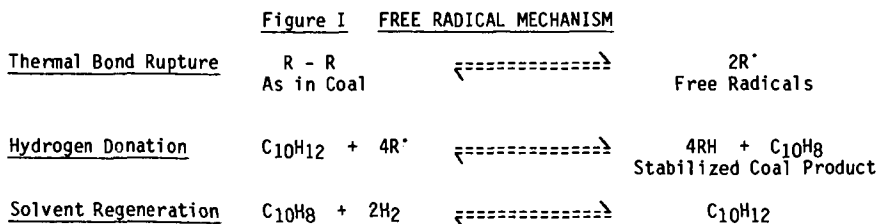
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INTRODUCTION

The ChemCoal Process utilizes chemical means to transform coal and other carbonaceous materials to solid, liquid, and slurry products. The process uses coal-derived solvents and aqueous alkali to dissolve and breakdown carbonaceous materials. Carbon monoxide is used to generate hydrogen via the water gas shift reaction to cap organic species. Insoluble sulfur and ash impurities are separated from the soluble organic fraction. Recycle solvent, light oils, alkali, and water are extracted from the soluble fraction and preasphaltenes (PA) and asphaltenes (A) are precipitated by the addition of methanol. The precipitated PA and A, the ChemCoal solid products, have been slurried and used in a diesel engine. The methanol fraction is processed to recovery recycle solvent, alkali, water, light oils, and methanol. The process has been evaluated under continuous process operation at the University of North Dakota Energy Research Center (UNDERC). A 10 TPD demonstration plant is proposed and will be sited near Powhatan Point, Ohio.

CLASSICAL THERMAL PROCESSES

Classical direct coal liquefaction processes involve high temperature thermal treatment of coal to rupture chemical bonds producing free radical coal fragments. The free radical fragments are stabilized by capping with hydrogen of a coal-derived solvent usually represented as Tetrahydrodecalin (THD), $C_{10}H_{12}$. This is represented as Figure I.



The classical process requires temperatures and pressures of approximately 425°C and 2500 psig. In the SRC process thermal bond rupture, hydrogen donation and solvent regeneration are carried out simultaneously in the liquefaction reactor. The hydrogen gas treatment rate may be 20,000 SCF/ton of coal feed with a consumption of 4,000 SCF/ton of coal.

Competing free radical reactions, not shown in Figure I, can occur resulting in recondensation of the free radical coal fragments and degradation of the hydrogen shuttle species. Hydrogen shuttle species are converted to degradation spe-

cies which do not lend themselves to regeneration. Conditions which favor the hydrogen donation reaction do not necessarily favor solvent regeneration. The EDS process attempts to overcome the solvent degradation and regeneration limitations by use of a separate catalytic regeneration reactor.

IONICALLY-AIDED CONVERSION

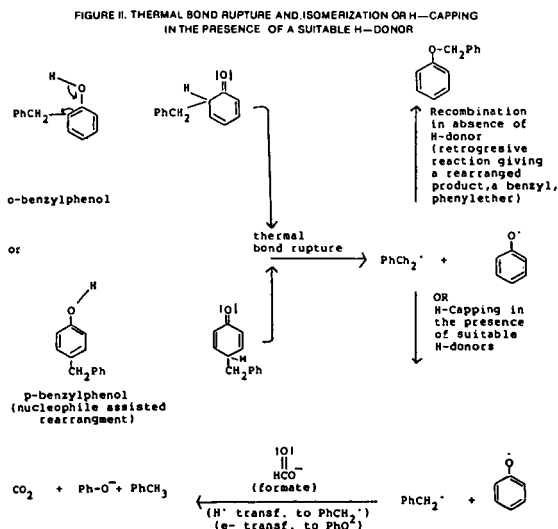
The chemical transformation of coal, by the ChemCoal Process, may make use of ionic chemistry while benefiting from low temperature thermal bond rupture mechanisms. Ionic reactions are represented in Figure II.

ChemCoal Process mechanisms may benefit from both ionic and thermal processes. The keto form of the o-(hydroxyphenyl)phenylmethane, OPPM, shown in Figure II is more easily formed into toluene and phenol than the enol form. The C-C bond shown by 'x' in II decreases in strength from 86 to 46 kcal/mol. This decrease in bond strength, due to a shift from sp^2-sp^3 to sp^3-sp^3 bondings as well as its allylic position with respect to the oxygen atom, is correlated to a decrease in activation energy over unassisted bond cleavage. The major effect of a nucleophile such as PhO^- is to facilitate proton transfer in keto/enol tautomerisms. The bond may then be broken homolytically at a lower temperature. Keto-enol tautomerisms may be ionically aided leading to the low temperature thermal bond rupture.

The role of the PhO^- and formate mechanism in the ChemCoal Process has been reported by Porter and co-workers.⁽¹⁾ The role of oxygenates on hydrocarbon bond dissociation has been reported by McMillen and co-workers.⁽²⁾⁽³⁾⁽⁴⁾

In the ChemCoal Process the transformation of coal is achieved at about 325°C and 1250 psig in the presence of phenolics, added alkali and water, and carbon monoxide. The requirement for tetralin or other hydrogen shuttles does not exist. Hydrogen plays a part in the conversion but an external source of hydrogen is not required, as the hydrogen is supplied from the water and CO.

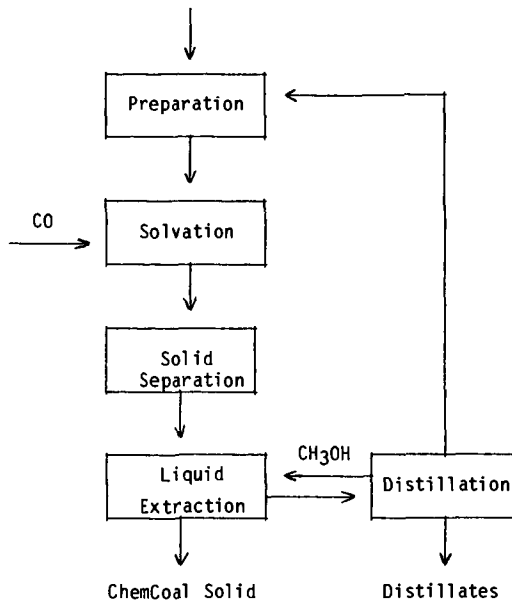
Under the ChemCoal processing conditions, the water gas shift reaction (WGSR) is promoted. It has been observed in the laboratory that those conditions which promote the WGSR do not necessarily promote transformation of coal. Therefore, it is assumed that there is a competing reaction but the presence of hydrogen and the formate ion are beneficial.



PROCESS DESCRIPTION

The ChemCoal Process involves the following five steps shown in Figure III:

Figure III ChemCoal Process Schematic



Preparation:

The coal is crushed and mixed with recycle solvent.

Solvation:

The coal slurry is heated to about 325°C in the presence of syngas at approximately 1250 psig. The preheater and reactor design incorporates a slow heating rate and a means to maintain S/C ratios in the reactor.

Solid Separation:

The slurry is centrifuged to remove the solids.

Liquid Separation:

The filtrate is treated with methanol to extract phenol, water, and alkali. The ChemCoal solid precipitates and is separated from the liquid phase.

Distillation:

The liquid phase is distilled to recover methanol, distillates, and recycle solvents.

PROCESS RESULTS

Table I summarizes the ultimate analysis of three ChemCoal Process coal-derived solid products. It is important to note that the coal-derived products are similar to No. 2 and No. 6 fuel oil in terms of sulfur, nitrogen, and ash content.

Table I ChemCoal Product Analyses Compared to Fuel Oils

Coal Rank: Source:	Lignite No. Dak.	Bituminous Ohio No. 6	Fuel Oil No. 6	Fuel Oil No. 2
Ash	0.19	0.12	0.01- 0.5	Nil
Carbon	83.5	86.06	86.5 -90.2	86.1-88.2
Hydrogen	6.41	6.11	9.5-12.0	11.8-13.9
Nitrogen	0.92	1.23	2.0	0.2
Sulfur	0.25	0.41	0.7- 3.5	.05- 1.0
Oxygen (diff)	8.73	6.07	2.0	Nil
HHV (Btu/lb)	15,400	15,700	17,400-19,000	19,000-19,750
1b Ash/MMBtu	0.115	0.076	0.005-0.30	Nil
1b SO ₂ /MMBtu	0.32	0.52	0.75-4.0	05.1.0

Other ChemCoal Product Properties (typical):

Autoignition Temperature 1100, \pm 30°F

Equilibrium Moisture 0.9%

Specific Gravity 1.03

Also of concern in the processing of coal is the sulfur and ash content of the products. Results obtained from a series of coals are summarized in Table II which shows that the products are very low in ash and sulfur content. In the case of an Eastern coal from the Sunnyhill Mine in Ohio (Ohio No. 6 seam), it is seen that the sulfur and ash content are reduced from 2.11 weight % to 0.41 weight % and 10.5 weight % to 0.12 weight %, respectively. In the case of the Western low-rank coal from the Indian Head Mine (Zap seam) of North Dakota, the sulfur and ash are reduced from 1.18 weight % to 0.25 weight % and 12.93 weight % to 0.19%, respectively.

Table II ChemCoal Process Results

Feedstock: Identification:	Coal Feed ^a		ChemCoal Product ^a		Percent Reduction	
	Sulfur	Ash	Sulfur	Ash	Sulfur	Ash
Ohio No. 6 (Sunnyhill)	2.11	10.5	0.41	0.12	80.6	98.9
North Dakota Lignite (Indian Head Mine)	1.18	12.93	0.25	0.19	78.8	98.1
Colorado Wadge (Energy Fuels II)	0.51	8.56	0.23	0.03	54.9	99.6
Texas Lignite (Big Brown)	0.85	14.10	0.07	0.07	91.8	99.5

^a Weight percent, on a moisture-free basis.

CONTINUOUS PROCESS UNIT (CPU) OPERATION

A continous process unit was operated at UNDERC under the ChemCoal processing mode. The unit is depicted schematically in Figure IV(5). Table III summarizes the operating conditions for the CPU test on an Indian Head Lignite. The CPU operated for 40 recycle passes. During passes 30-39, GC/MS data indicated the recycle solvent was approximately 95% coal-derived from the process.

Table IV summarizes the results from the recycle test. The results confirmed earlier batch conversion data, established operability of the process, and solvent balances.

FIGURE IV
The ChemCoal CPU Scheme

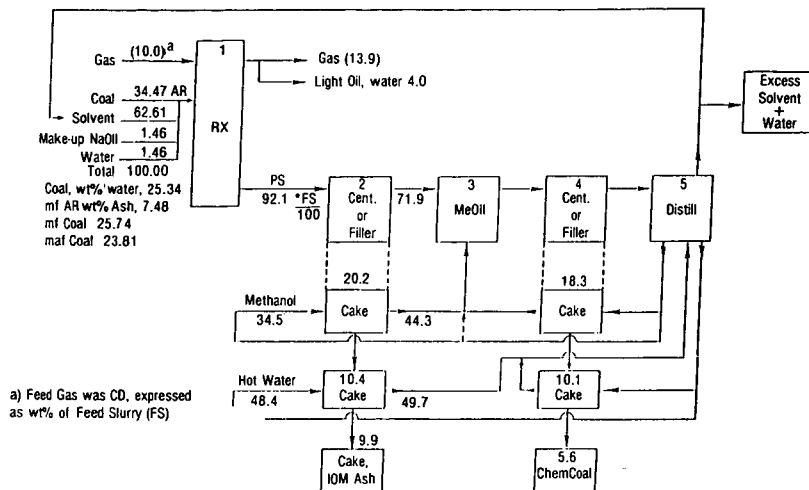


FIGURE 2.4. Developing Stream Data as wt% of Feed Slurry

Table III ChemCoal Recycle Test - Operating Conditions
Indian Head Lignite

- 1.8 solvent-to-coal ratio (2.5 lbs/hr)
- Alkali at 6% of MAF coal
- Preheater/reflux -- 250°C/1800 psi
- Reactor/reflux -- 340°C/1800 psi
- Syngas feed before reactors (7 SCFH)
- MEOH addition to PPT ChemCoal solids
- Centrifuge -- solids removal
- Distillation -- 19" VAC/100°C

Table IV ChemCoal Recycle Test - Results
Indian Head Lignite

- System operable for 40 recycle passes
- Solvent balance achieved
- Conversions -- ~ 85% MAF coal
- Reductant consumption (CO) in H₂ equivalents ~ 1.5% MAF coal
- Gas make -- ~ 2.0% MAF coal
- PA and A yield -- 50% MAF coal
- Distillate yield -- 30% MAF coal

DEMONSTRATION PLANT

An overall block flow diagram of a conceptual 10 TPD ChemCoal demonstration plant is shown in Figure V. A brief description of the processing steps is given in the following paragraphs.

The coal is received from storage, crushed and ground to 80% minus 200 mesh. The coal is then mixed with two parts of process-derived recycle solvent to one part coal and an amount of aqueous alkali.

The slurry mix is pumped to about 1500 psig through a heater/preheater/reactor system. In the presence of carbon monoxide, coal solvation occurs at about 340°C.

The reactor effluent mixture (gas, liquid, and solids) is separated in a phase separator. Residual liquids are condensed from the gas stream and returned to the liquid slurry streams. The gases are flared and scrubbed to remove noxious species.

The slurry stream is processed through a centrifuge to remove solids. The filter cake (centrifuge solids) is washed to recover process solvent constituents, which are returned to the process. The cleaned cake is rendered inert by heat treatment (pyrolyzed), all liquids returned to the process, and all gases (not shown) flared and scrubbed.

The filtrate (centrifuge liquids) are contacted with a recycle methanol stream. The ChemCoal solid product (coal-derived preasphaltenes and alphasphaltenes) precipitates when contacted with methanol. The precipitate is removed by centrifugation, washed, and stored for subsequent product testing. The liquid stream is distilled to recover recycle solvent, coal-derived distillate, and methanol.

ChemCoal Associates, a joint teaming arrangement between Carbon Resources, Inc., CRI Associates, Limited, and The North American Coal Corporation is planning to design, construct, and operate a demonstration plant at a facility near Powhatan Point, Ohio. The University of North Dakota Energy Research Center and the MK-Ferguson Company of Cleveland, Ohio are assisting ChemCoal Associates in this effort.

ACKNOWLEDGEMENTS

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